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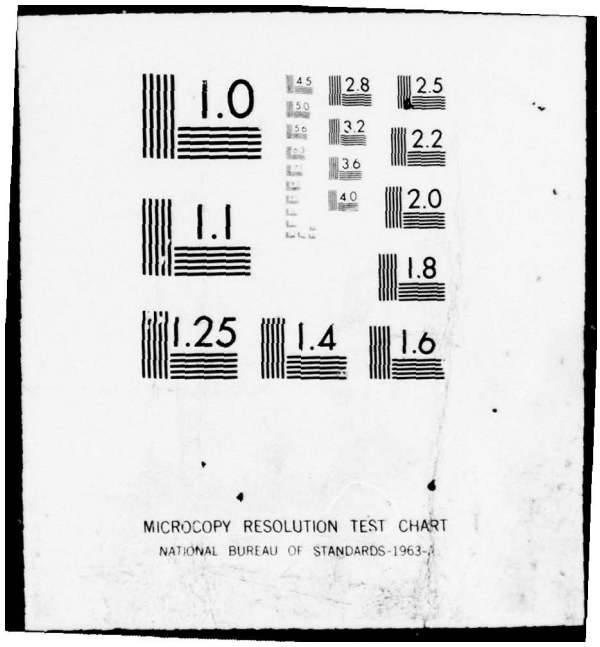
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REPORT SAMSO-TR-79-41

LEVEL II

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The Production of Chloramine by Liquid Phase Injection of Ammonia and Chlorine

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1 June 1979

Final Report

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This report has been reviewed by the Office of Information and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

Approved

J. F. Kephart

J. F. Kephart, Maj, USAF

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

FOR THE COMMANDER

Joseph D Nicoll

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The results of preliminary experiments on the injection of liquid reactants NH_3 and Cl_2 into a reactor to produce chloramine NH_2Cl are reported. The normal process for the anhydrous production of NH_2Cl introduces the reactants as gases. The direct injection of liquid reactants would be a simplification. Problems with the constancy of reactant delivery and dispersion of liquid reactants caused the observed yields to vary greatly. At NH_3/Cl_2 ratios of 3.3 all of the NH_3 was consumed in two experiments and dichloramine was detected in the analytical solutions. When the ratio was increased to 4.3,

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19. KEY WORDS (Continued)

20. ABSTRACT (Continued)

NH_3 was present in all cases and one experiment gave a yield of 60 percent NH_2Cl. No plugging of the injectors was observed in any of the experiments and continuous operation appeared feasible. The NH_4Cl product formed in large flakes that only weakly adhered to the reactor parts. The NH_4Cl settled out much more rapidly in the liquid injection experiments than in comparable gas phase injection experiments. The development of this approach should be considered.

CONTENTS

FIGURES

TABLE

I. INTRODUCTION

Chloramine NH_2Cl is used in the synthesis of hydrazine, unsymmetrical dimethylhydrazine and monomethylhydrazine. The Raschig synthesis produces chloramine by the reaction

$$NH_3 + OCl^- \rightarrow NH_2Cl + OH^- \qquad (1)$$

in aqueous ammonia-caustic solution. The appropriate amine and additional base are then injected into the reaction stream and flash heating produces the appropriate hydrazine. This reaction requires dilute solutions because of attack by NH_2Cl on the products. A way of increasing the concentration of product in the reaction stream is to produce NH_2Cl under anhydrous conditions in the gas phase. This approach has been developed by Sisler and coworkers (Refs. 1 through 7). Studies of the gas phase reaction

$$2NH_3 + Cl_2 \rightarrow NH_2Cl + NH_4Cl(s) \qquad (2)$$

and the effects of temperature, diluent gases, and flow rates are contained in a previous report (Ref. 8).

The gas phase production of NH_2Cl on an industrial scale requires the vaporization of large quantities of NH_3 and Cl_2, and the delivery of these gaseous reactants under high pressure and temperature. The gaseous injectors, reaction zone, and the gases must be further heated to approximately 300° C to prevent fouling of the system by NH_4Cl. Previous work has shown that high yields of NH_2Cl are produced at lower temperatures before fouling by NH_4Cl takes place (Refs. 6, 8), and that lower temperatures may increase the yields. An excess of NH_3 over the stoichiometric quantity or an additional diluent gas is required (Refs. 1, 6 through 8).

The direct injection of liquid reactants would be preferable on a large scale. The cooling resulting from the vaporization of reactants might permit reactions with smaller excesses of NH_3 and with no gaseous diluent. In addition, the nature of the NH_4Cl product might be advantageously changed. An exploratory investigation of the direct injection of liquid reactants is reported.

II. EXPERIMENTAL

The apparatus, which was adapted from previous gas phase experiments (Ref. 8), is shown in Figure 1. The reactant lines were all 316 or 304 stainless steel (SS) except for polyethylene transfer lines from the flowmeters to the liquid reactant storage tubes. The reactor was a 2 l Pyrex resin kettle. Known amounts of the reactants were condensed in the storage tubes by immersing the tubes in a bath at dry ice temperatures and allowing the reactants to flow into the reservoirs at known flow rates for measured periods of time. After the reactants had warmed to above 0° C, 98 psig (777 kPa) of helium pressure was used to drive the liquids upward through 3 mm tubing to lengths of 0.25 mm ID 316 SS capillary tubing and into the reactor. It was necessary to prechill the lines carrying reactants to assure reproducible delivery times. The insert in Figure 1 shows the injector arrangement. NH_3 flowed from the upper tip downward around the Cl_2 injector. Reacted gases were disposed of in a water scrubber.

The flow rates of both NH_3 and Cl_2 were controlled by varying the length of the capillary tubing. Attempts were made to control the flow rates using constant lengths and variable driving pressures of inert gas with the reactants cooled to 0 to -30° C. Both "vapor lock" and solidification of the reactants in valve orifices prevented the use of this approach. The NH_3 vapor pressure at room temperature is approximately 100 psig and that for Cl_2 is somewhat lower. Therefore, by using a driving pressure of 98 psig and slightly cooling the reactant lines, the liquids could be delivered with predictability. Calibration of the capillaries was performed by observing the time required to deliver known amounts of the reactants. The calibration curves for NH_3 and Cl_2 are shown in Figure 2. The flow rates of the reactants were the slopes of the regression lines through the points. The flow rates were generally reproducible to better than ±15 percent.

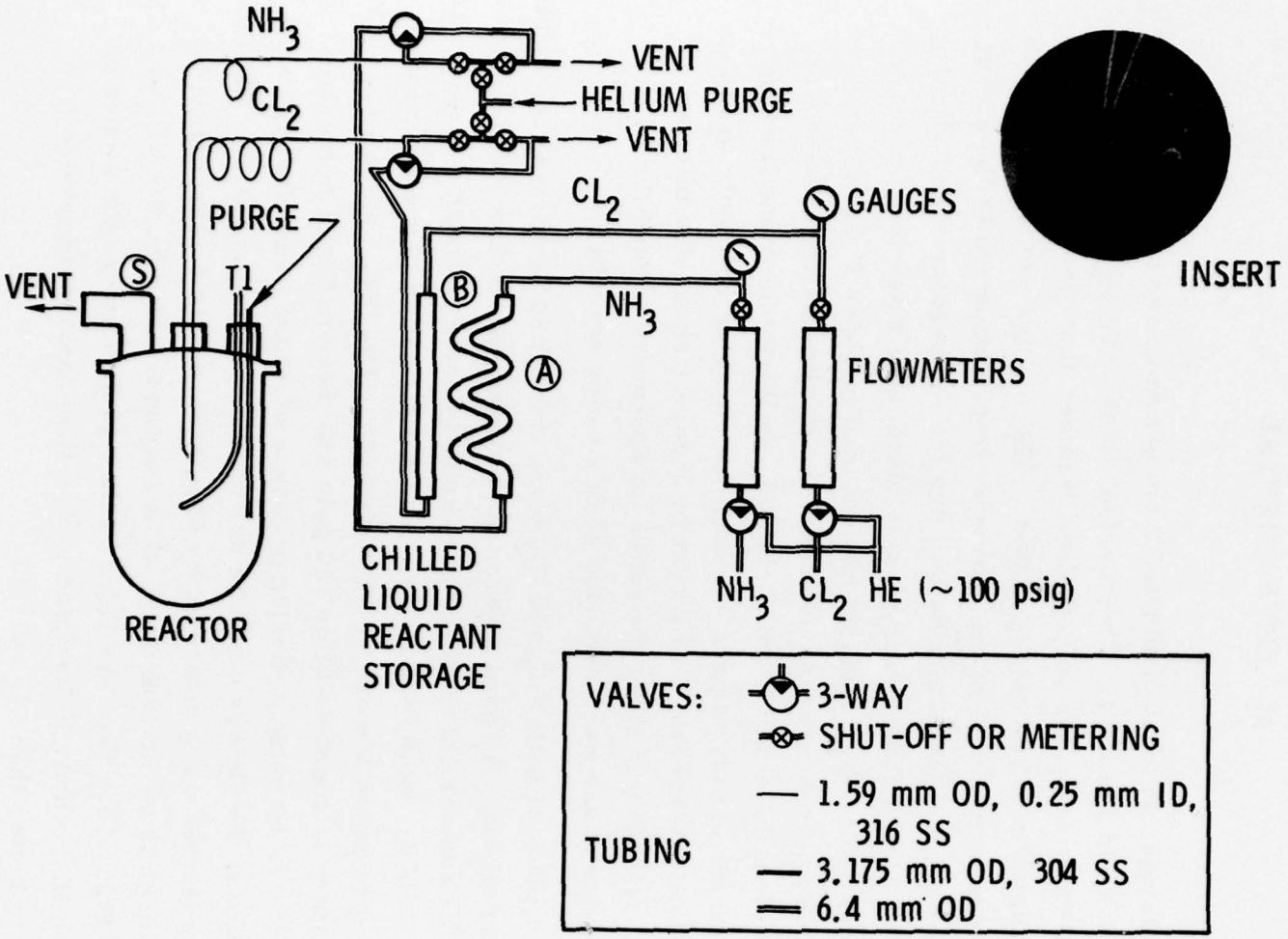


Figure 1. Apparatus used for the liquid injection of reactants for the production of chloramine. The reactants were injected through 0.25 mm ID capillary tubing. S is the sampling port. A and B are the metered liquid reactants storage vessels for NH_3 and Cl_2 respectively. They could be immersed in a -78°C bath. Insert is a photograph of the injector with liquid Cl_2 spraying from the lower tip.

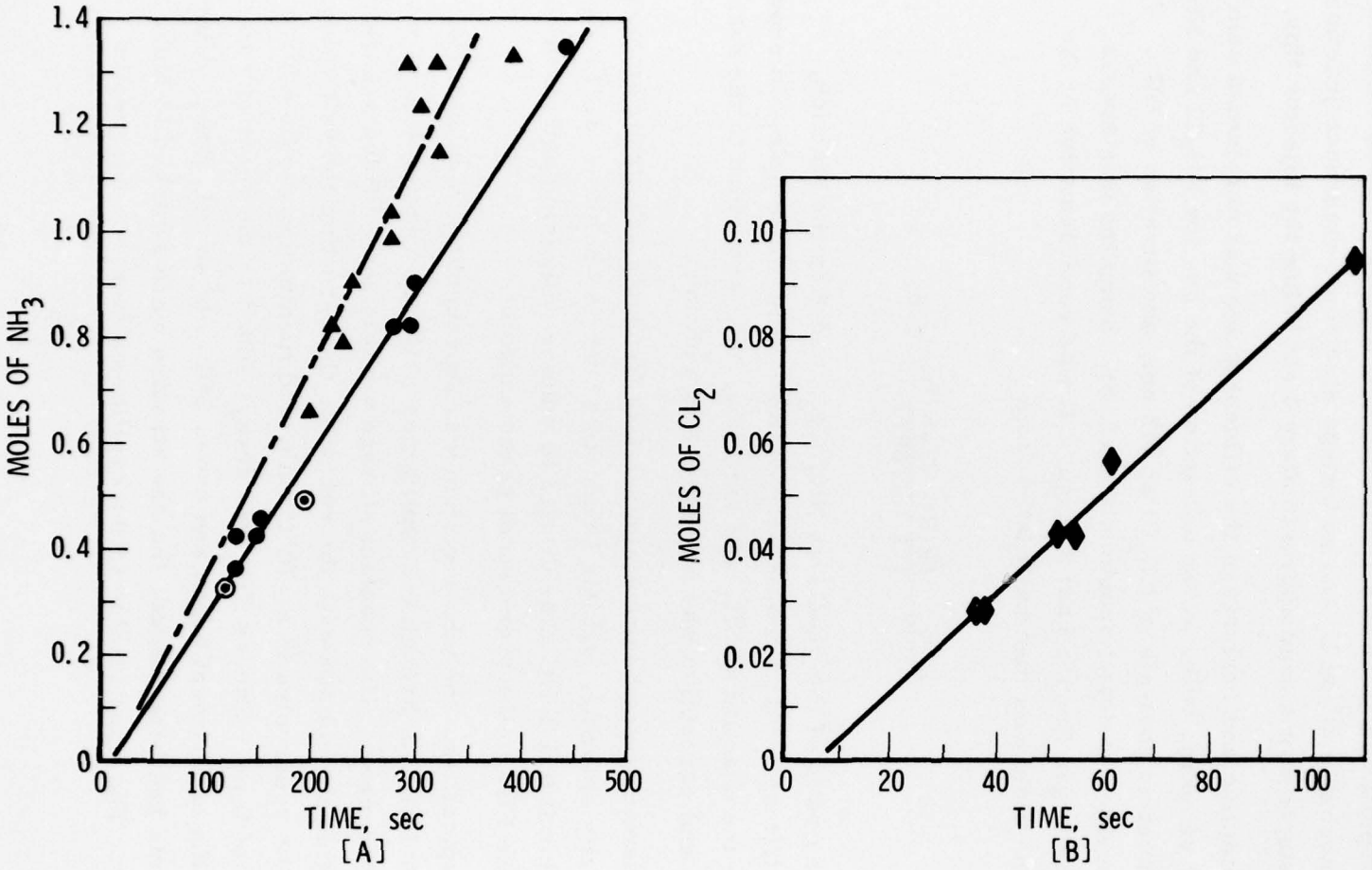


Figure 2. Calibration curves for reactant delivered vs. time for 0.25 mm ID capillary tubing. Reactants were forced through tubing with 98 psig of helium pressure. [A] NH_3 calibration and regression lines for 2.53 m (▲, – - –) and 3.3 m (●, ——) long tubes. [B] Cl_2 calibration and regression for 1.5 m long tube.

The temperature at T1 was recorded using a glass encased chromel-alumel thermocouple (Type K) and an Omega electronic reference junction. The thermocouple was placed approximately 4 cm below the injector tips.

The sampling and analysis of the effluent gases was performed using an evacuated sampling bulb, water extraction of the gas for NH_2Cl and NH_3, spectrophotometric analysis of NH_2Cl at 243 nm, and titration of NH_3. This has been described in detail previously (Ref. 8). Sampling was always delayed until the gas flowing past S (Figure 1) was representative of the reaction. The yield was then calculated from

$$\text{Yield} = \left(\frac{E(R - 2.667)}{1 - 1.667E}\right) X\ 100 \qquad (3)$$

where R is the ratio of the reactants NH_3/Cl_2, and E is the fraction, moles NH_3Cl/(moles NH_3 + moles NH_2Cl) (Ref. 8) in the sample. In experiments where the quantity of NH_3 was very low, NH_3 was added to the extraction solution and correction was made for this addition.

The chemicals used were Matheson Gas Products anhydrous ammonia and High Purity chlorine, and Air Products grade "A" helium. J. T. Baker Company Dilut-it 0.1 N HCl was diluted to volume with deionized water and used to titrate NH_3 to the bromcresol green endpoint.

In a typical run, the whole system was thoroughly purged with He. The purge was maintained through the capillaries while the reactants were measured and condensed. The reactant storage vessels were loaded separately by first purging the volume with the reactant, then shutting the exit valve, immersing the reservoirs in a -78° C bath, and monitoring the flow for a fixed period of time. Excess NH_3 was always added to the reservoir to assure that the experiment began and ended with only an NH_3 flow. After each reservoir had been loaded, the gas streams were switched to high pressure He. The lines leading to the capillaries from the reservoirs

and part of the capillaries were then chilled by pouring cold isopropyl alcohol over alumina wool insulation that had been wrapped around the tubing. An experiment was initiated by opening the NH_3 valve to the capillary, waiting until liquid was observed in the reactor, and then opening the Cl_2 valve. Although the reaction would run indefinitely, the Cl_2 quantity limited reaction times to approximately 200 sec. To assure initiation of the reaction at the low temperatures of the liquids, the reactions were run with illumination from several fluorescent tubes. The temperatures were recorded. A sample was collected from the sample port approximately 90 sec after Cl_2 liquid was delivered. Approximately 45 sec were required to collect a sample. After the reaction had terminated and a He flow was re-established, the sample was extracted and analyzed as previously described.

III. RESULTS AND DISCUSSION

The objective of these experiments was to determine if Cl_2 and NH_3 could be reacted by injecting the liquid reactants. The points of importance were the production of NH_2Cl, the nature of the NH_4Cl produced, and the demonstration that the reaction occurred predictably. The last point was of concern because initiation of the reaction could have been delayed if it is a free radical/atom mechanism and an explosion could have resulted. In all cases the reaction initiated and ran smoothly.

A summary of the results of experiments at two different NH_3/Cl_2 ratios is given in Table 1. Chloramine was produced at both reactant ratios in significant quantities although not reproducibly. The scatter in the yield data was the result of several problems. The largest contributor was probably variations in the liquid delivery rates. The reactant ratios and the uncertainties are from the calibrations in Figure 2. These calibrations, however, are based on the integrated flow times for known quantities of liquid and do not reflect the undetectable variations in liquid flow rates during this period. During calibrations, "spurting" of the reactants was observed. The data are reasonable if the flow rate of one or both of the reactants varied because the probability of dropping below the stoichiometric ratio of 2 NH_3 to 1 Cl_2 was less at the higher NH_3 flow rate.

The experiments at the lower ratio of reactants gave indication that less than the stoichiometric ratio was at times present and that decomposition of the products was occurring. In two cases, experiments 1 and 5, no NH_3 was detected in the samples although excess NH_3 should have been present even if all of the NH_2Cl had decomposed by the reaction

$$2\ NH_3 + 3\ NH_2Cl \rightarrow N_2 + 3NH_4Cl \qquad (4)$$

Table 1. Summary of Experiments on the Injection of Liquid Reactants to Produce Chloramine

No.	Flow Ratio NH_3/Cl_2	Temperature T1 (°C)	Yield (%)	Comments
1	3.30 ± .36	--	--	NH_2Cl detected, no NH_3 detected
2	3.30 ± .36	70	39	
3	3.30 ± .36	70	2	
4	3.30 ± .36	70	19	
5	3.30 ± .36	80	(25)	NH_2Cl detected (est. yield), no NH_3, detected $NHCl_2$
6	4.29 ± .53	(105)	60	Temperature was unstable and rising
7	4.29 ± .53	(180)	35	
8	4.29 ± .53	(70)	28	

Dichloramine $NHCl_2$ was detected in experiment 5 in at least minor amounts by the ultraviolet absorption of the analysis solution near 310 nm (Refs. 8 through 10). Chloramine was reasonably concentrated in this sample, but no NH_3 was present. Under these conditions, the pH is quite low and $NHCl_2$ may have formed in the water solution rather than in the reactor (Ref. 10).

The temperature below the injector was stable at the lower reactant ratio. The temperature at the higher ratio was rising during the entire reaction period and sometimes reached as high as 200° C. The temperatures given in the table are averages during the sample period. The use of liquid reactants did appear to lower the temperature of the reaction when compared with similar temperature probe positions and flow rates in gas phase injection experiments (Ref. 8).

Experiment 6 shows that acceptable yields of NH_2Cl are possible by this technique. It is clear that for this approach to be practical, the mechanical problems of liquid delivery and injector design must be attacked. An additional problem may be that cold NH_4Cl particles may promote decomposition (Ref. 6). The evaporation of the liquid reactants on NH_4Cl particles could result in subambient temperatures.

The reaction of NH_3 with Cl_2 has been proposed to occur by a free radical/atom chain reaction. The generation of Cl atoms

$$Cl_2 \rightarrow 2\ Cl \tag{5}$$

would initiate the process and a chain reaction would produce NH_2Cl.

$$NH_3 + Cl \rightarrow NH_2 + HCl \tag{6}$$

$$NH_2 + Cl_2 \rightarrow NH_2Cl + Cl \tag{7}$$

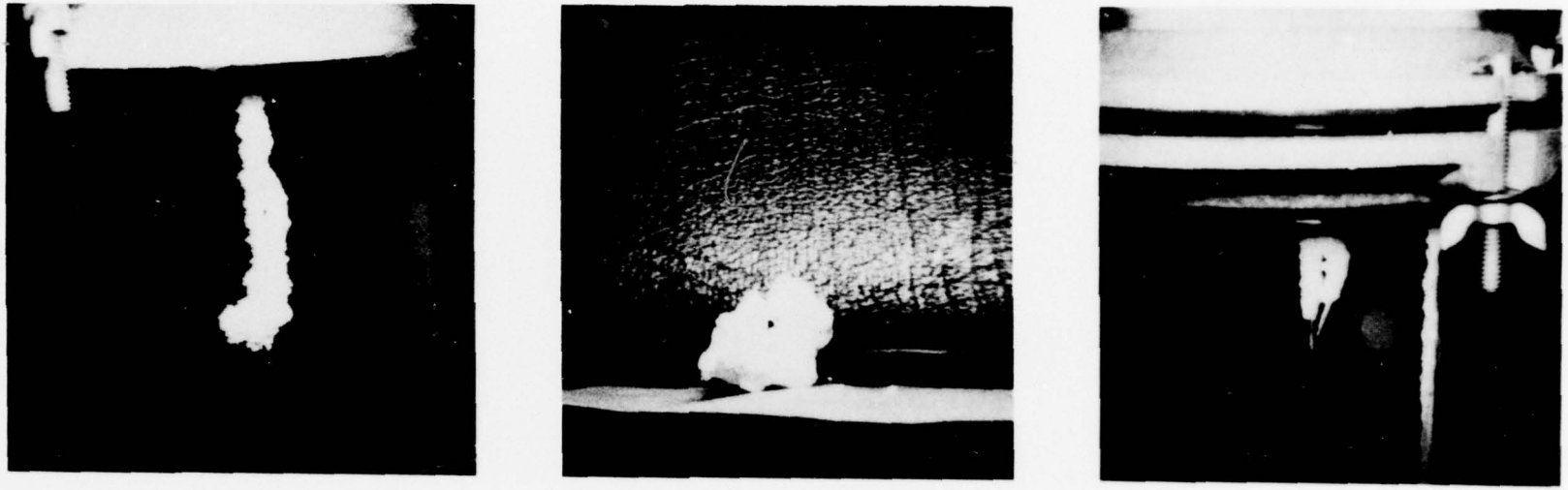
Reactions of NH_2, NH, and Cl with each other would then cause chain termination and lowered yields. High radical and atom concentrations would decrease the chain lengths and the yields of NH_2Cl. The evaporating droplets of reactants in the liquid injection case could provide high local concentrations of radicals with disproportionate ratios of Cl to NH_2. This could cause higher temperatures and decreased yields. The greatest dispersion and mixing of the reactants would appear to be beneficial. The use of a small jet of diluent gas would perform this task and perhaps increase the yields as was the case in the gas phase injector experiments (Ref. 8).

The most encouraging observations from these experiments were the nature of the NH_4Cl solids and the operation of the reactor. Although NH_4Cl was blown all over the reactor and tended to hang on any surface, the density of the particles was such that most of it settled to the bottom of

the reactor immediately. Generally, the NH_4Cl was flake-like with larger, more granular crystals than the material in gas phase experiments.

Figure 3 shows photographs of the NH_4Cl that adhered to the injectors. These deposits were fluffy and easily removed. Note that Figures 3A and 3B show no glassy deposits although they are in the immediate area of the mixing of reactants. There was also a difference in the appearance of the NH_4Cl between the higher and lower reactant ratio experiments. The flakes of NH_4Cl were larger in the experiments with higher reactant ratios and had a definite "wet" appearance. Most significantly, mild vibration of the reactor tips caused the deposit to fall away as shown in Figure 3C. A thin, adherent, dust-like coating of NH_4Cl covered all internal parts of the reactor but no heavy buildups were observed.

All experiments ran smoothly; flow variations during the reaction could not be observed due to the NH_4Cl cloud. No plugging of the injector tips occurred at any time during the experiments. Consecutive experiments were performed by purging with He and cleaning the reactor to permit observation of the next experiment. No tip cleaning was ever necessary. This is in contrast to the gas phase studies at room temperature (Ref. 2), where the injector frequently plugged and the reaction zone and injector required careful cleaning between experimental runs (Ref. 8). The liquid injection reactor appeared to be capable of continuous operation with no more than occasional vibration to free the injector of nonadherent NH_4Cl buildup.



[A] [B] [C]

Figure 3. Photographs of the NH_4Cl buildup on the liquid injector assembly.
[A] at the termination of an experiment.
[B] NH_4Cl formation removed from the injector, viewed from the top. Note the fluffy appearance and the openings where the liquids were expelled.
[C] The injector tips after mild vibration were clean of NH_4Cl.

IV. SUMMARY

The reaction between NH_3 and Cl_2 to produce NH_2Cl was found to be feasible when the reactants were injected as liquids. The reaction probably still occurs in the gas phase. The NH_4Cl produced was more readily separated from the product gas stream with liquid reactant injection than in gas phase injection experiments in the same reactor. The NH_4Cl was less adherent and mild vibration would remove buildup from the injectors. No plugging of the injectors was ever observed.

The yields were variable and not very high in the experiments at reaction ratios of NH_3 to Cl_2 of 3.3 and 4.3. At the lower reaction ratio all NH_3 was consumed in two experiments. One experiment at the higher ratio gave a yield of NH_2Cl of 60 percent. The low yields and the complete consumption of NH_3 indicate that variations in the delivery rate were occurring and that dispersion of the liquid droplets was insufficient.

The advantages of liquid reactant delivery and the observations made in this work indicate that chloramine production by this technique is an attractive alternative to gas phase reactant injection. The problems of flow variation could be corrected easily on a larger scale unit and reactant dispersion could be improved by the use of a diluent gas jet.

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